Efficient Rechargeable Li/O_2 Batteries Utilizing Stable Inorganic Molten Salt Electrolytes

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Liox Power, Inc. – Caltech – LBNL

2017 DOE Vehicle Technologies Program Review

June 5-9, 2017

Project ID: ES233

Overview

Timeline

- Project start date: Oct 2014
- Project end date: Sept 2017
- Percent complete: 83%

Budget

- Total project funding
  - DOE share: $1,050K
  - Liox share: $375K
- Funding received
  - FY16: $286K DOE, $154K Liox
  - FY17: $116K DOE, $63K Liox

Barriers

- Barriers addressed for Li/air batteries
  - Electrolyte stability
  - Voltage hysteresis
  - Air tolerance

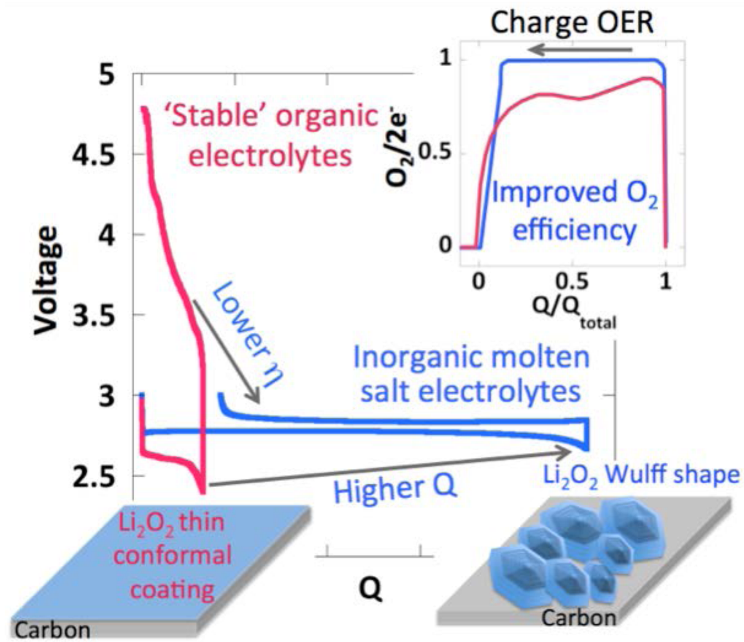
Partners

- LBNL
  - In situ characterization and mechanistic analysis
- Caltech
  - Nanostructured materials

Project Objective and Relevance

Objective

- To demonstrate the first practically stable electrolyte for Li-air batteries and thus eliminate a barrier to high cycle life
- To solve the problems of high voltage hysteresis, low rate capability and low areal capacity of Li/O_2 cells by operating at elevated temperature and using an inorganic molten salt electrolyte that solubilizes discharge products
- To provide a cell and system that can operate robustly in ambient air without O_2 purification



Comparison of voltage profiles and discharge product morphologies for Li/O_2 cells using molten salt (blue) and DME organic electrolyte (red) *(Giordani et al. JACS, 2016)*

Relevance

- All organic electrolytes evaluated to date are insufficiently stable
- High voltage hysteresis, low rate capability and low areal capacity in current Li/O_2 cells arises from low solubility and sluggish charge transport in discharge products
- Intolerance to ambient air necessitates cumbersome and costly air purification

Milestones

FY16

Q1 Quantify e^-/O_2 and OER/ORR ratio for metals and metal alloys in half cells under pure O_2 (Dec. 15) **Complete**

Q2 Determine the kinetics and mechanisms of electrochemical nitrate reduction in the presence of O_2, H_2O and CO_2. Synthesize electronically conductive ceramics and cermets (Mar. 16) **Complete**

Q3 Quantify e^-/O_2 and OER/ORR ratio for electronically conductive ceramics and cermets in half cells under pure O_2. Go/No-Go: Demonstrate e^-/O_2=2 and OER/ORR ratio=1, +/- 5%. Criteria: Correcting for the effect of Li_2O_2 crossover (Jun. 16) **Complete**

Q4 Demonstrate solid electrolytes that are stable to molten nitrate electrolytes over a temperature range of 100 °C to 150 °C for 6 months or greater (Sep. 16) **Complete**

FY17

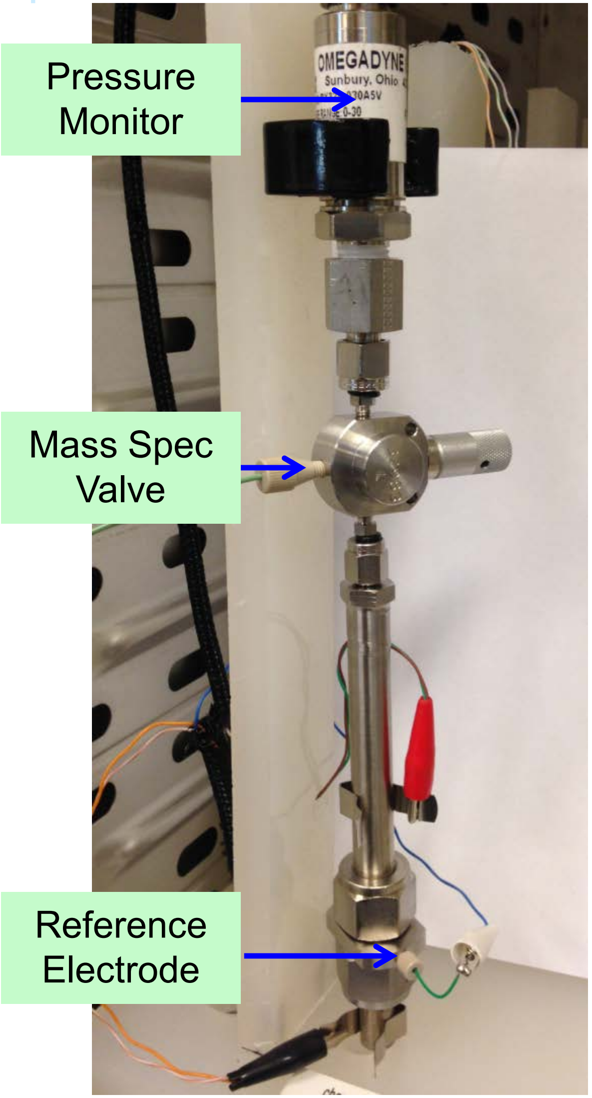
Q1 Demonstrate discharge specific power and power density ≥ 800 W/kg and ≥ 1600 W/L, respectively, based on air electrode mass and volume. Measure interfacial resistance as a function of temperature, current density and cycle number in Li/Li symmetric cells (Dec. 16) **Complete**

Q2 Scale-up downselected cell components for 4 mAh and 10 mAh cells (Mar. 17) **Complete**

Q3 Demonstrate ≥10 cycles at ≥ 90% round-trip energy efficiency in laboratory-scale Li-air cells comprising a molten nitrate electrolyte and protected Li electrode (Jun. 17) **Ongoing**

Q4 Fabricate and test 4 and 10 mAh cells (Sep. 17) **Ongoing**

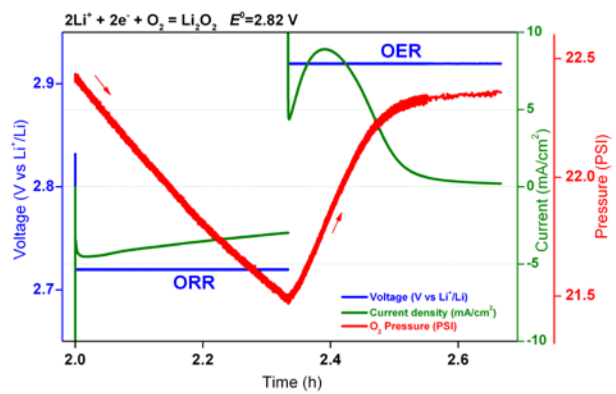
Approach



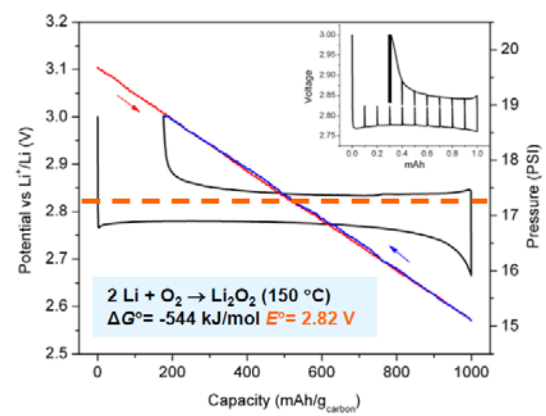
- **<u>Approach</u>:** Replace volatile, unstable and/or air-intolerant aqueous or organic electrolytes with inert molten nitrate electrolytes and operate cell above liquidus temperature (> 80 °C)

- **<u>Strategy</u>:** Improved reversibility and rate capability since discharge products (Li_2O_2, Li_2O, LiOH and Li_2CO_3) are stable and sparingly soluble in molten nitrate electrolytes; Electrode kinetics and mass transport are faster at elevated temperature

- **<u>Research methodology</u>:** Combine quantitative gas analysis (pressure monitoring, mass spectrometry) with precise coulometry to analyze air electrode processes



Constant potential cycle

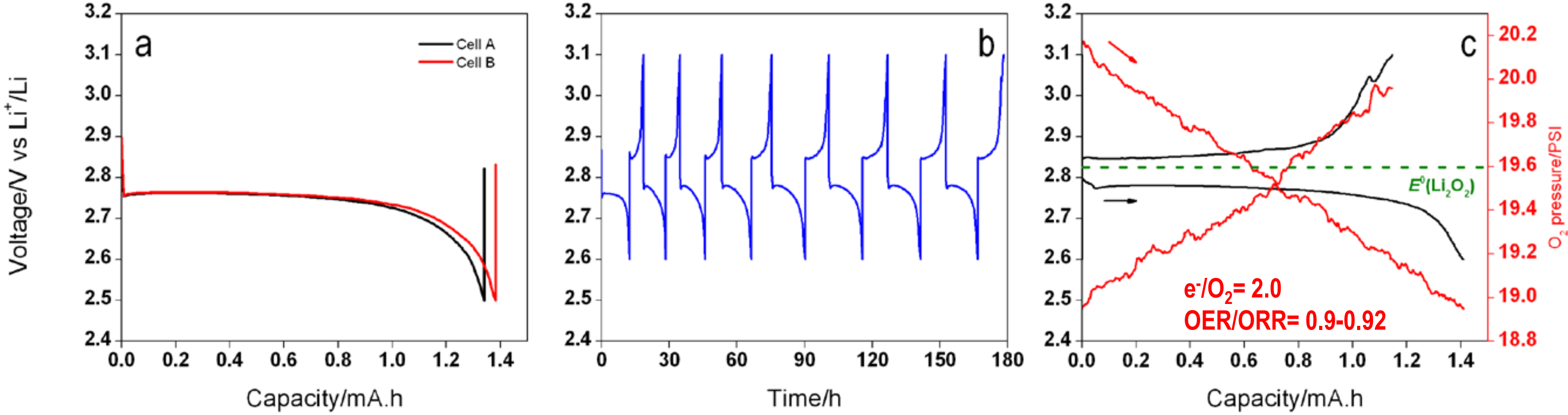


Constant current cycle

Accomplishments

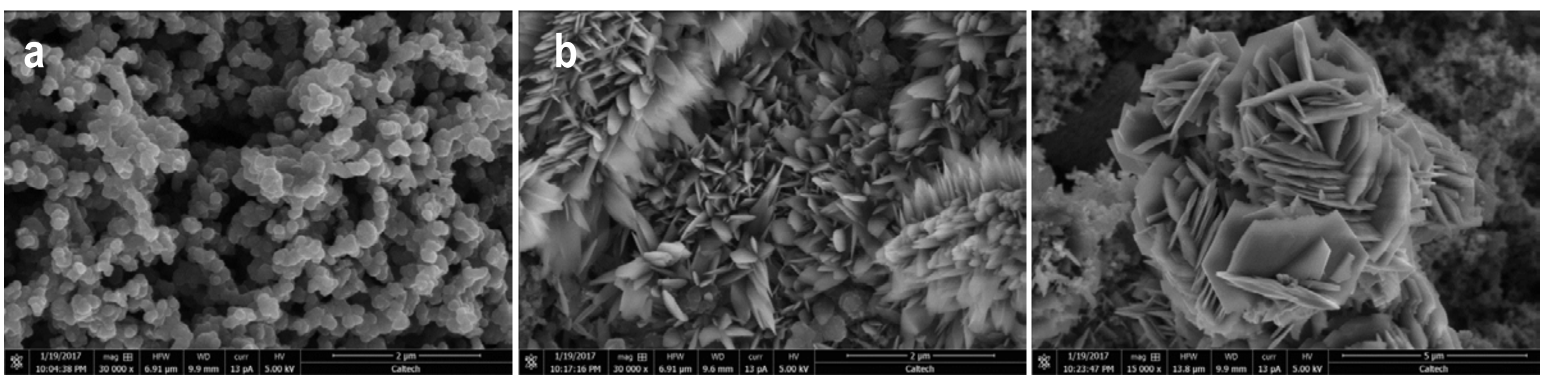
Air cathode material stability (Milestone 2.3.4)

Improved stability of Boron Carbide (B_4C) compared to Super P carbon and IrO_2



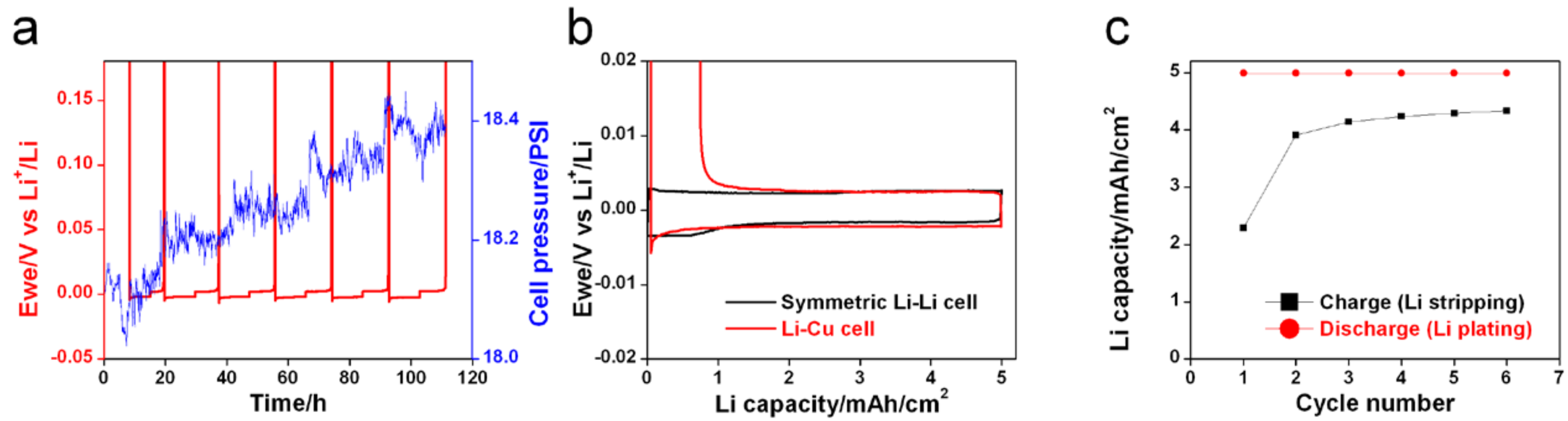
a) Galvanostatic discharge curves for Li/O_2 cell containing a $LiNO_3$-KNO_3 electrolyte and a B_4C-based air electrode (T= 150 °C, P_{O_2}= 1.4 atm, j= 0.32 mA/cm^2) b,c) Cycling profile of a molten nitrate Li/O_2 cell containing a B_4C air electrode (T= 150 °C, j= 0.13 mA/cm^2, m_{B_4C}≈ 5 mg/cm^2)

SEM Analysis of Boron carbide air cathode: a) OCV b) discharged to 2.6 V at 0.13 mA/cm^2



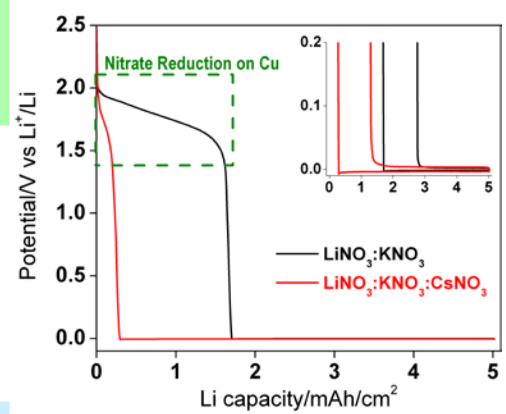
Accomplishments

Characterize Li metal/molten nitrate interface



a) Li plating/stripping onto Cu (A_{Li}=A_{Cu}=0.502 cm^2) at j= 0.5 mA/cm^2, at 150 °C, under Ar, in $LiNO_3$-KNO_3 melt b) Cycling curve comparison between Li-Li symmetric cell and Li-Cu cell employing $LiNO_3$-KNO_3 melt, at 0.5 mA/cm^2 c) Li capacity per cycle number

- Low interfacial resistance of Li metal with $LiNO_3$-KNO_3: ≈1 Ω·cm^2
- Pressure rise and gas evolution (nitric oxide and nitrogen confirmed with MS) due to parasitic reaction of the nitrite anion with lithium metal
- Low Coulombic efficiency for Li stripping/plating (≈87%)



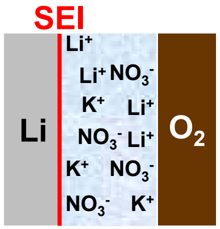
Li plating on Cu: 1st discharge comparison between $LiNO_3$-KNO_3 and $LiNO_3$-KNO_3-$CsNO_3$ melts (0.5 mA/cm^2, 150 °C, Ar, 10% Li utilization, 5 mAh/cm^2)

<u>Proposed approaches to improving Li metal/molten nitrate interface:</u> Cs^+ additives[1] and lithium protection using chemically and thermally stable Garnet solid electrolytes.

[1]Zhang et al. *J. Phys. Chem. C* **2014** *118* (8) 4043–4049

Accomplishments

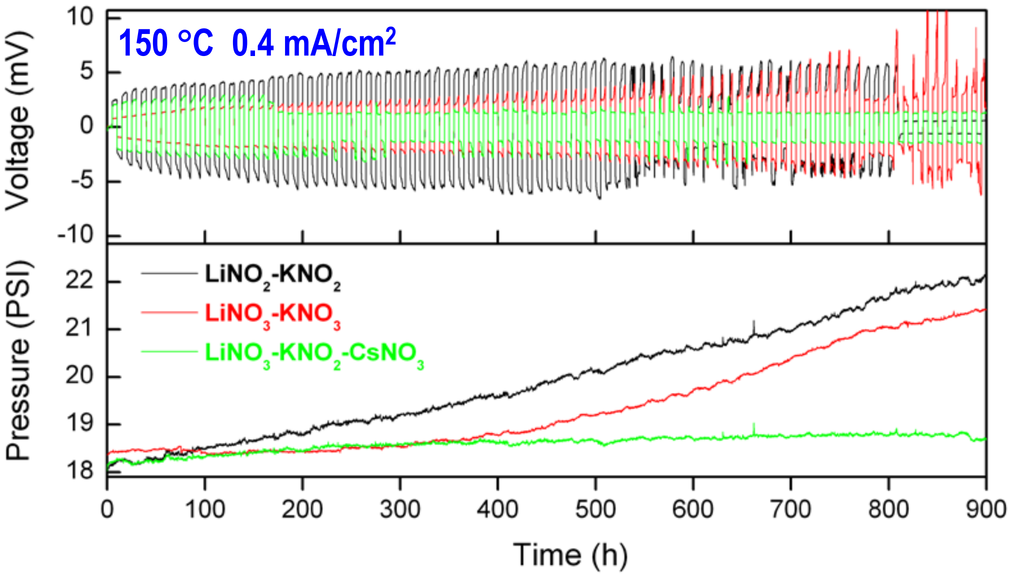
Improved Li metal/molten nitrate interface with Cs^+ cations



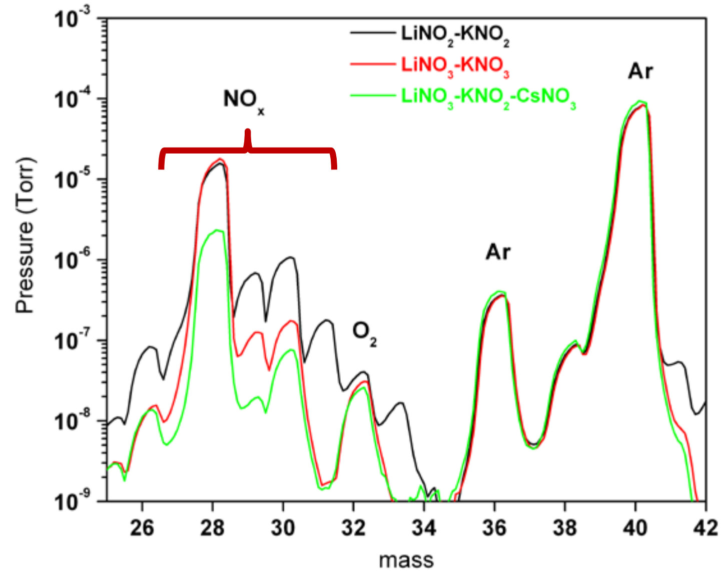
Anode SEI reaction: $NO_3^-(sol) + 2Li(s) \rightarrow Li_2O(s) + NO_2^-(sol)$

Cs^+ suppresses NO_2^- reduced by Li metal to form NOx gas

Li/Li symmetric cell cycling (top) with *in situ* pressure analysis (bottom)



MS analysis of cycled cells (100 cycles)

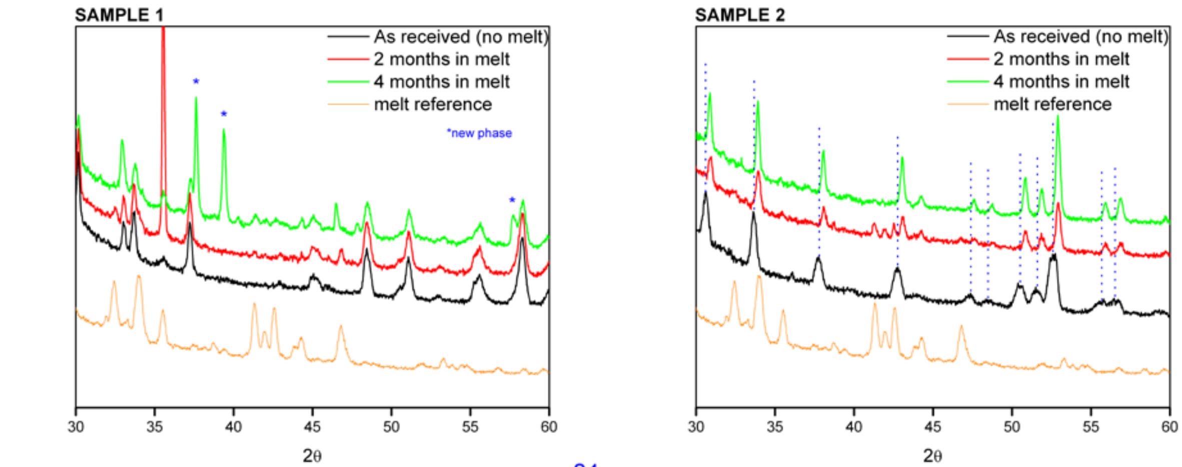


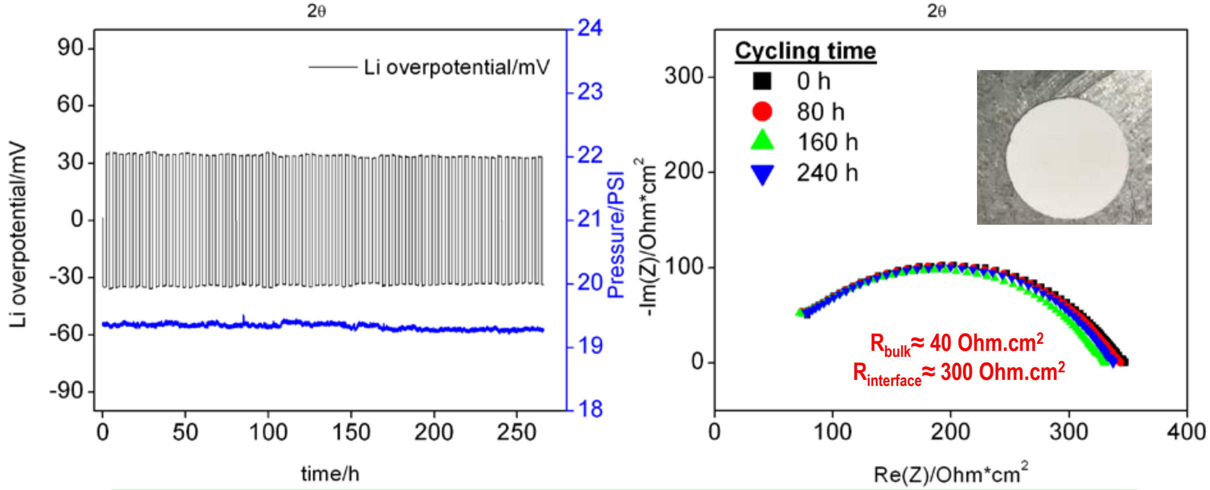
- Addition of $CsNO_3$ salt to the melt inhibits electrolyte decomposition by Li metal.
- No pressure rise due to NO_x formation or increase in overpotential in cell with $LiNO_3$-KNO_2 $CsNO_3$ eutectic.
- Overpotential increase and NO_x evolution in cells using electrolyte formulations without Cs^+.

Accomplishments

Molten Nitrate-Stable Solid Electrolytes (Milestones 3.1.1-3.1.3)

XRD study of LATP (left) and LLZO (right) immersed in $LiNO_3$-KNO_3 melt at 150 °C





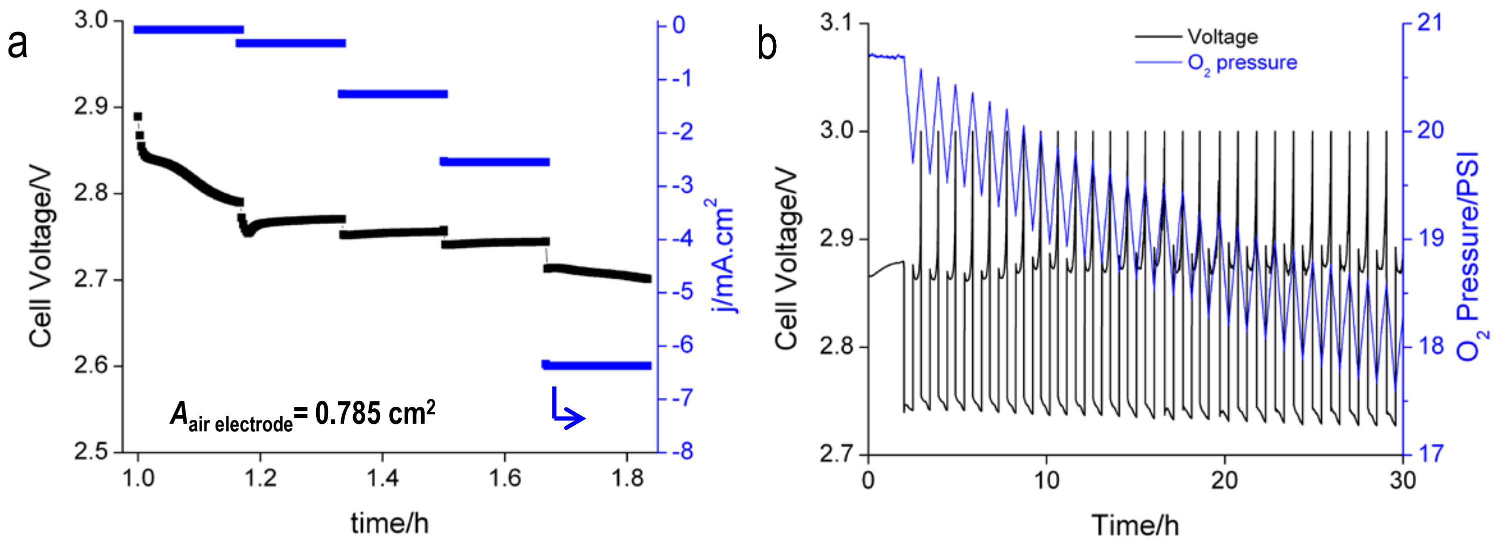
(Left) Li/Li symmetric cell cycling at 185 °C under Ar using LLZO solid electrolyte (j=0.1 mA/cm^2, 4 h per cycle) (Right) EIS recorded intermittently during cycling

- Appearance of new peaks following exposure of LATP to molten nitrate indicates chemical instability.
- Diffraction pattern of LLZO is unchanged following months of exposure to nitrate melt.
- Interfacial resistance is unchanged in Li/LLZO/Li cell stored at OCV at 185 °C for 50 days.
- Stable Li metal/LLZO interface during cycling at 185 °C at 0.1 mA/cm^2.

Accomplishments

High Power Oxygen Cathode (Milestone 2.4.1)

a) Molten nitrate Li/O_2 cell discharge voltage profile at 150 °C as a function of current density
b) Li/O_2 cell cycling in $LiNO_3$-KNO_3 at 150° C at 2.5 mA/cm^2 current density (≈500 mA/g_{carbon})



Air cathode: Super P Carbon:PTFE (95/5wt%)
Mass= 4 mg (carbon + binder)
Volume= 7.8 mm^3 (1 cm diameter, 100 microns thick)

Cell voltage at 5 mA discharge current: 2.7 V

P (W) = U (V)*I (A) = 2.7*0.005 = 13.5 mW

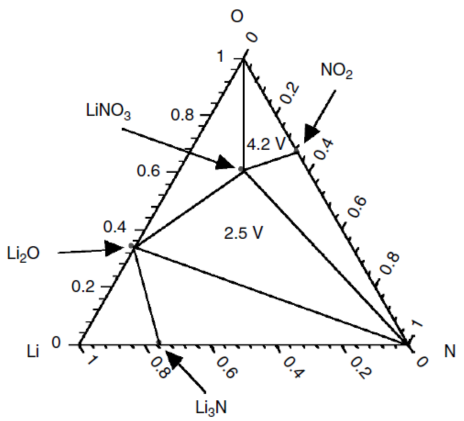
Discharge Specific Power = 3375 W/kg
Discharge Power Density = 1730 W/L

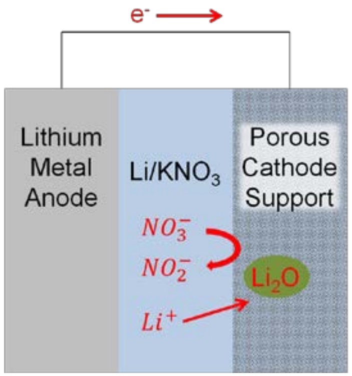
- Relatively high rates (up to 6.3 mA/cm^2, 1250 mA/g of cathode) were achieved for both discharge and charge half-cycles, emphasizing the fast kinetics associated with O_2 electrochemistry at elevated temperatures in a molten nitrate electrolyte.
- IrO_2 and B_4C cathode materials do not support current densities greater than 0.5 mA/cm^2. We hypothesize that this difference is due to different wettability and/or lower surface area compared to Super P.

Accomplishments

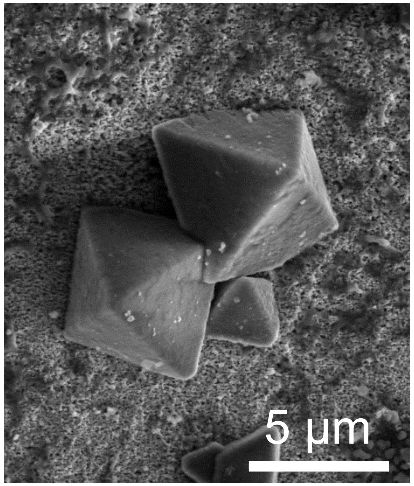
Novel High Energy Density Cathode Chemistry Based on Oxyanion Redox

$$2Li^+ + 2e^- + NO_3^- \overset{\text{catalyst}}{\leftrightarrows} Li_2O + NO_2^- \quad E^0=2.5V$$

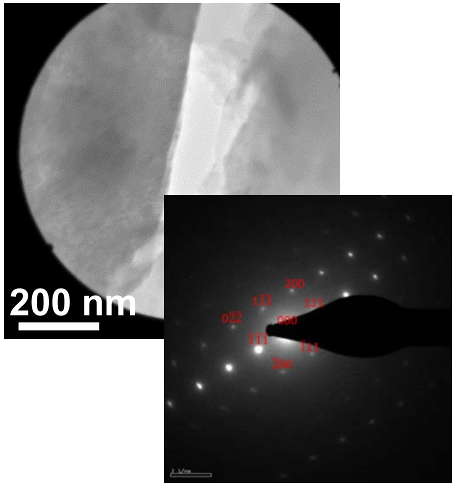




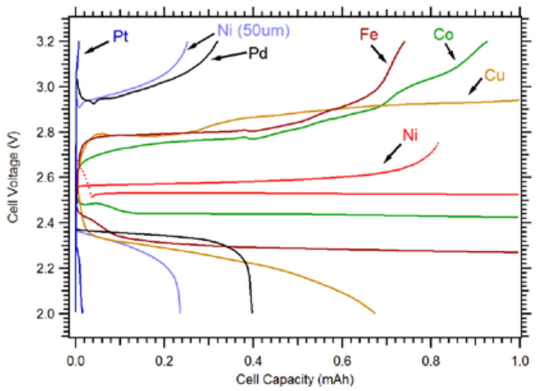
SEM Li_2O



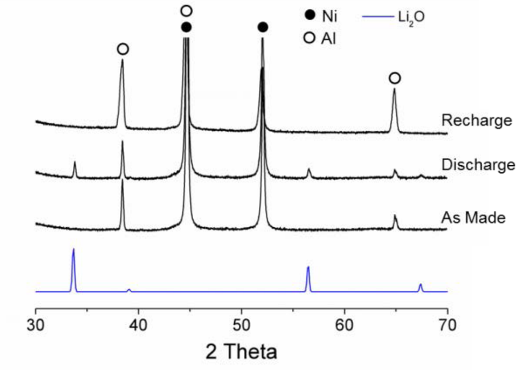
TEM Li_2O

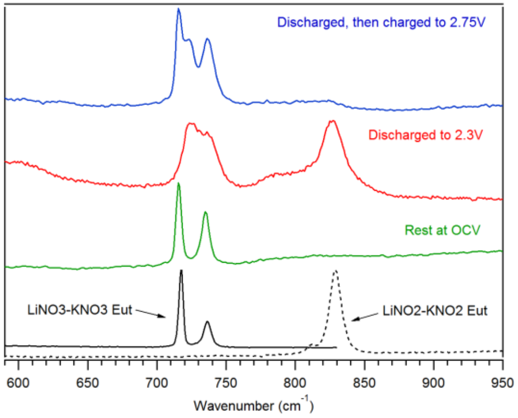


Catalyst screening: Nickel nanoparticle catalyst enables reversible cycling at 0.25 mA/cm^2.



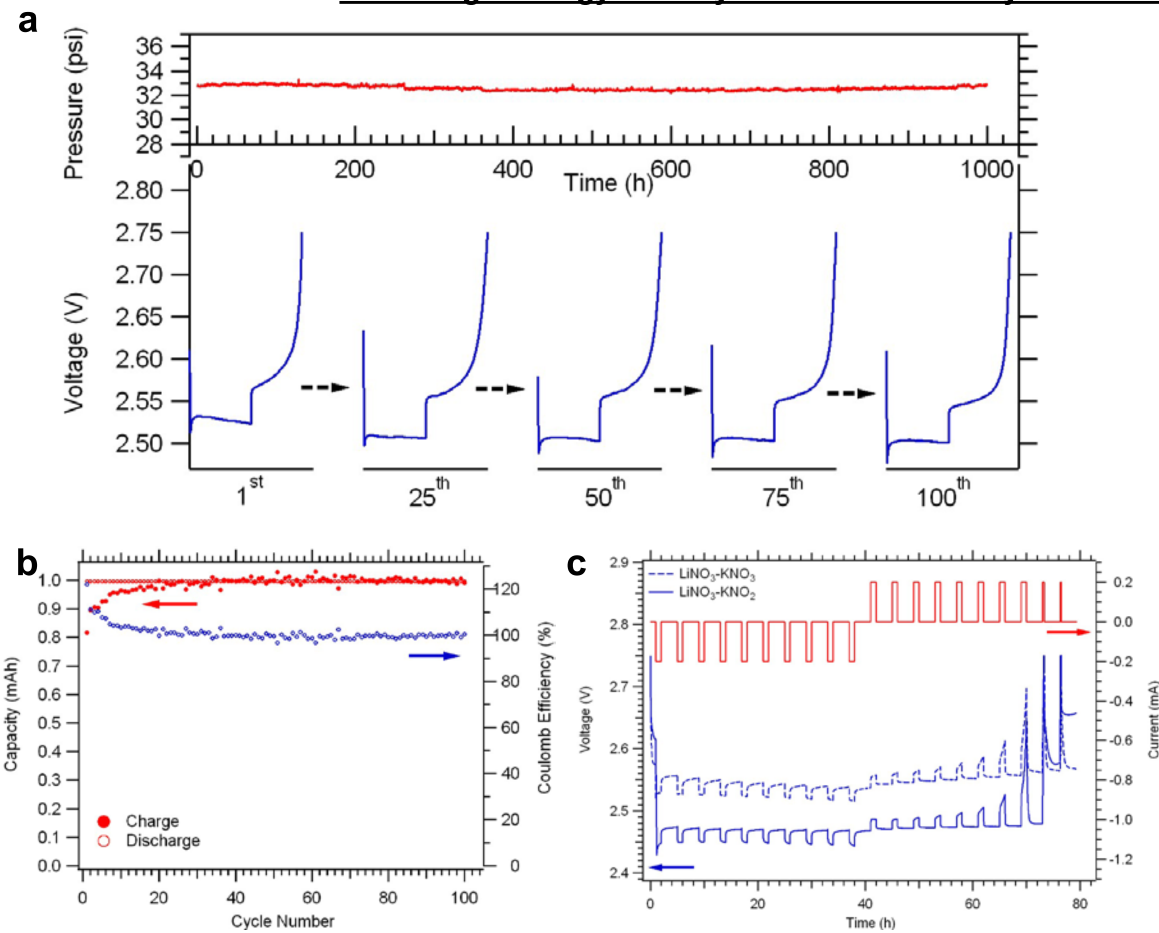
XRD / Raman Across Full Cycle





Accomplishments

Novel High Energy Density Cathode Chemistry Based on Oxyanion Redox



a) Long-term cycling using nitrate oxyanion redox cathode catalyzed by Ni nanoparticles (150 °C at 0.25 mA/cm^2)
b) Capacity vs Cycle Number with coulombic efficiency
c) GITT demonstrates rapid relaxation to equilibrium cell voltage of ~2.5 V for $2Li^+ + 2e^- + NO_3^- \leftrightarrows Li_2O + NO_2^-$ proposed battery reaction, consistent with calculated standard emf of the cell

- >100 cycles achieved using catalyzed oxyanion conversion cathode.
- No parasitic NO_x evolution observed via internal cell pressure monitoring.
- Anion exchange chromatography of electrolyte quantitatively confirms formation and decomposition of nitrite on discharge and charge, respectively.
- Challenge: demonstrate high cathode utilization (high discharge capacity) per mass of molten nitrate active material.
- Approach: Use of solid electrolyte + Contain molten nitrate within cathode (catholyte).

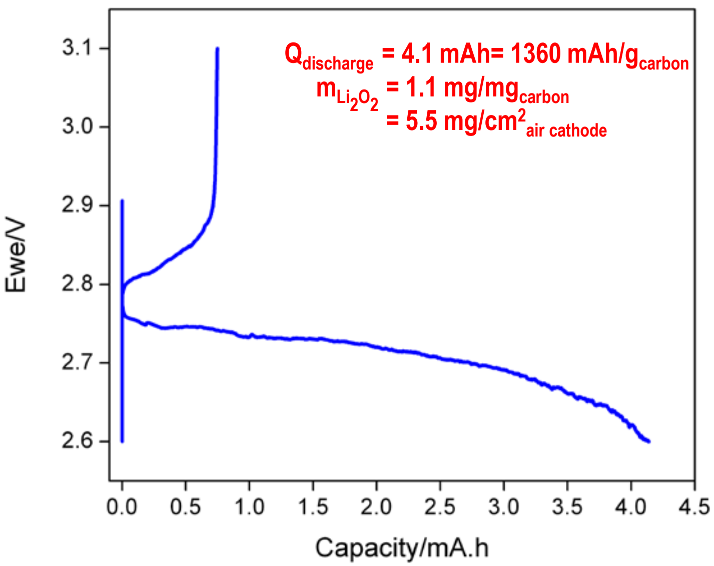
Accomplishments

High Capacity LLZO-protected Li metal cells using O_2 and oxyanion redox cathode chemistries (Milestone 2.4.2)

O_2 electrochemistry

Cathode reaction: $2Li^+ + 2e^- + O_2 = Li_2O_2$

***Eeq* ≈ 2.8 V / E_{theo} = 3270 $Wh/kg_{Li_2O_2}$**

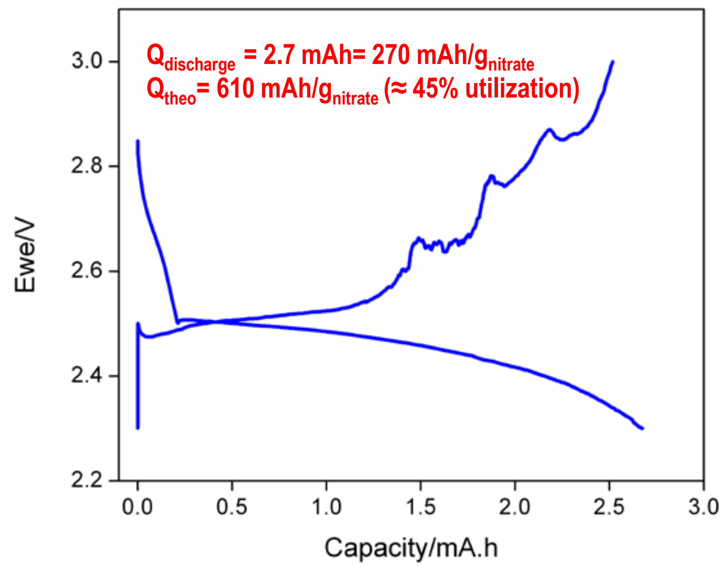


Li/O_2 cell voltage profile at 185 °C using Super P Carbon:PTFE (95:5 wt.%) cathode at 0.05 mA/cm^2 current density (m_{carbon}= 3 mg, $m_{nitrate}$= 6.5 mg)

NO_3^- electrochemistry

Cathode reaction: $2Li^+ + 2e^- + NO_3^- = Li_2O + NO_2^-$

***Eeq* ≈ 2.5 V / E_{theo} = 1525 $Wh/kg_{eutectic}$**



Molten nitrate Li cell voltage profile at 185 °C using nanoporous nickel cathode (Ni:$LiNO_3$-KNO_3 eutectic 50:50 wt.%) at 0.05 mA/cm^2 current density (m_{Ni}= $m_{nitrate}$= 10 mg)

- High temperature (185 °C) used to reduce ASR and eliminate dendrite growth using LLZO electrolyte.
- Relatively high discharge capacity in O_2 cell (1360 mAh/g of carbon, ~6.5 mAh/cm^2).
- High temperature accelerates carbon decomposition in O_2 cell leading to poor reversibility.
- Demonstrated 45% active material utilization (nitrate anion reduction) with high reversibility.

Collaboration and Coordination with Other Institutions

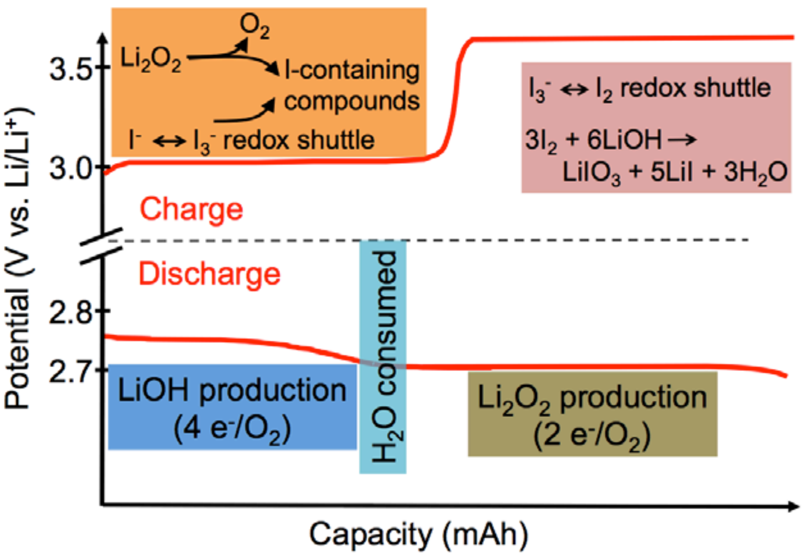
- **Lawrence Berkeley National Laboratory**
  - Prof. Bryan D. McCloskey: In situ characterization and mechanistic analysis

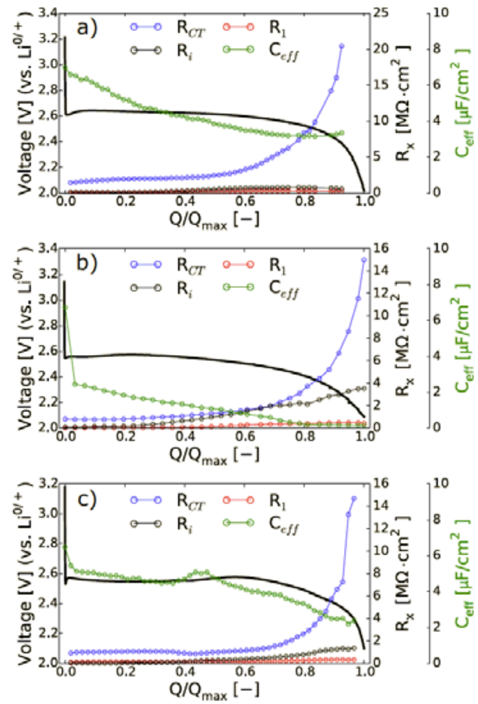
- **California Institute of Technology**
  - Prof. Julia R. Greer: Nanostructured materials

Collaboration and Coordination with Other Institutions (LBNL)

4 electron ORR using redox mediation (Milestone 2.3.5) and fundamental EIS studies

Impedances as measured using electrochemical impedance spectroscopy and quantified using porous electrode theory





LiI enables e/O_2=4 when H_2O is present (carbon electrode). OER/ORR ratio <1 and e/O_2<4 on charge

Burke et al., ACS Energy Letters, 2016, 1(4), 747-756

0.1M LiTFSI in DME electrolyte, porous XC72 carbon air cathode

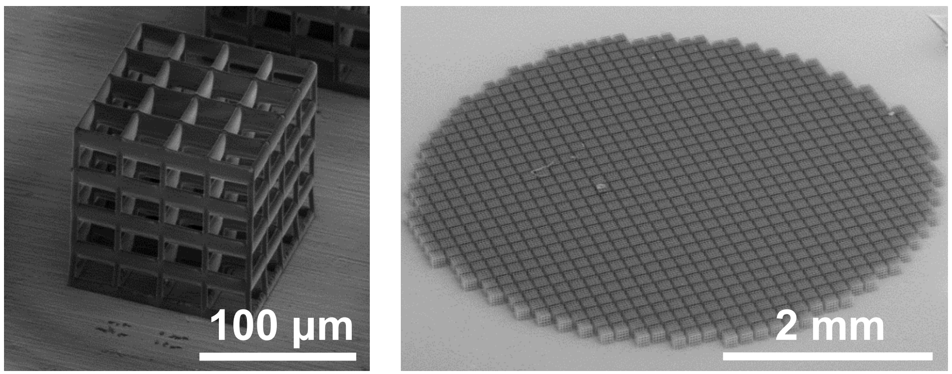
Charge transport resistance (R_{ct}) always dominates over ionic resistance (R_i), Li anode interfacial resistance (R_1)

Knudsen et al., J. Electrochem. Soc., 2016, 163(9), A2065-71

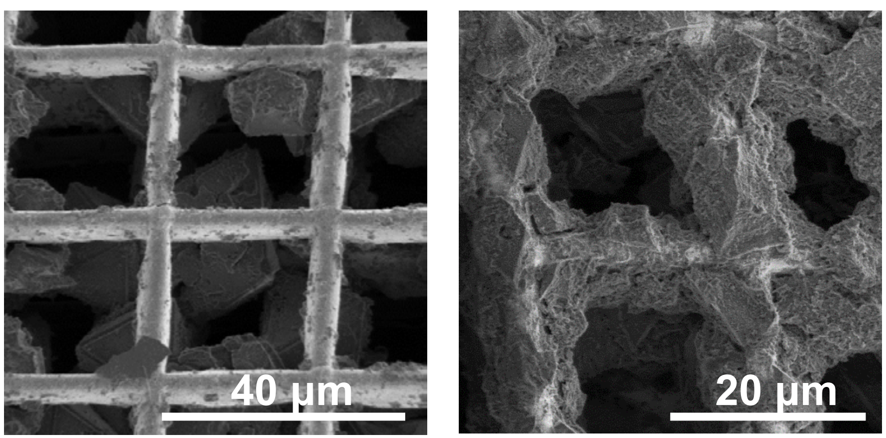
Collaboration and Coordination with Other Institutions (Caltech)

Demonstration of 3D Electrode for Crystal Growth Accommodation (Milestones 2.4.1 and 2.4.2)

5mm Diameter Nickel Architected Electrodes

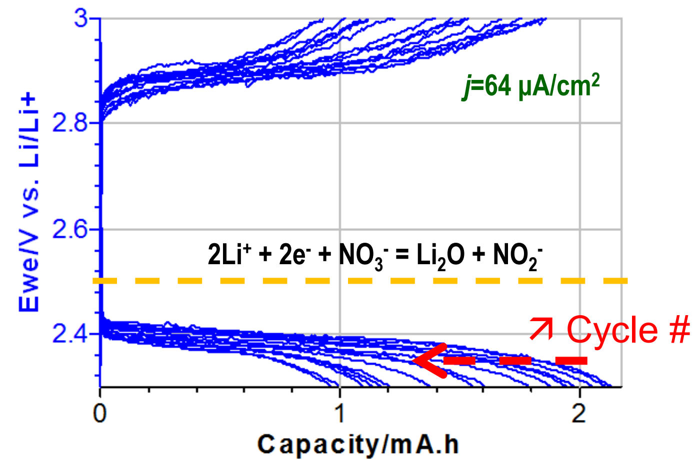


Li_2O Growth in Pore Volume of Lattice Electrode



- Precise control of pore size and geometry allows exact understanding of the effect of air electrode structure on capacity and rate capability.
- Architected electrode demonstrates significant capacity with low surface area for a phase forming chemistry.
- High rate capability and utilization per unit mass of Ni catalyst (>250 mA/g, >10,000 mAh/g).

Reversible Nitrate Electrochemistry



Remaining Challenges and Barriers

- Demonstrate high rate (1 - 3 mA/cm^2) of Li stripping/plating using LLZO or solid electrolyte at 100-150 °C.
- Demonstrate cycling in cells scaled-up to 4 and 10 mAh cells (Milestones 4.1-4.3) for both O_2 and oxyanion redox cells.
- Increase practical capacity (areal, gravimetric, volumetric) including active and inactive components for both O_2 and oxyanion redox cells.
- 4 electron O_2 cycling, i.e. find catalysts able to form lithium oxide reversibly.
- Engineer efficient elevated temperature thermal management and system designs for EV applications.

Future Work – FY2017

Demonstrate Prototype Molten Salt Li-Air Batteries

❑ **Go/No-Go:** Demonstrate ≥10 cycles at ≥90% round-trip energy efficiency in laboratory-scale Li-air cells comprising a molten nitrate electrolyte and protected Li electrode **(Jun. 2017)**

❑ Fabricate and test 4 and 10 mAh cells **(Sep. 2017)**

Any proposed future work is subject to change based on funding levels

Summary

- Identified O_2 electrode materials with improved stability in molten nitrates at 150 °C (e.g. Boron Carbide).
- Suppressed parasitic reaction between molten salt and lithium metal using Cs^+ additive.
- Identified LLZO as stable solid electrolyte for lithium protection in molten nitrate.
- Identified and confirmed novel rechargeable oxyanion redox cathode chemistry.
- Demonstrated high specific power and capacity using structured cathode materials.
- All milestones achieved to-date.

Thank you very much to the DOE Office of Vehicle Technologies for your support!